DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 197

CEMENTING QUALITIES OF THE CALCIUM ALUMINATES

BY

P. H. BATES, Chemist

Bureau of Standards

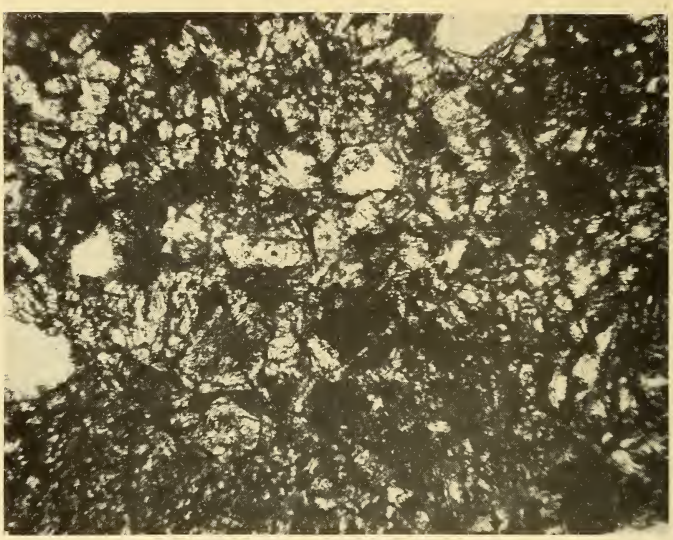
Reference book, not to be taken from the Library.

SEPTEMBER 27, 1921

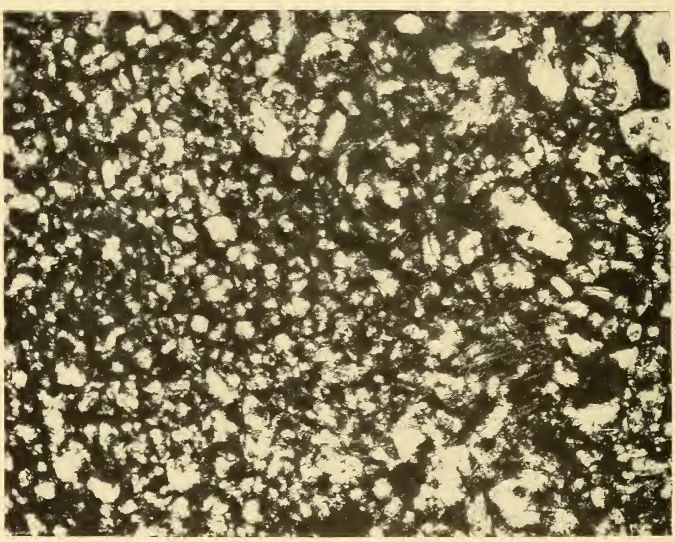
PRICE, 10 CENTS

Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1921



a



b

FIG. 1.—*Sections of typical Portland cement clinker, showing lack of distinct outline of the constituents.* (*a*) × *115;* (*b*) × *135*

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 197

CEMENTING QUALITIES OF THE CALCIUM ALUMINATES

BY

P. H. BATES, Chemist

Bureau of Standards

SEPTEMBER 27, 1921

PRICE, 10 CENTS

Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1921

CEMENTING QUALITIES OF THE CALCIUM ALUMINATES

By P. H. Bates

ABSTRACT

The four calcium aluminates ($3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, $3CaO.5Al_2O_3$) have been made in a pure condition and their cementing qualities determined. The first two reacted so energetically with water that too rapid set resulted to make them usable commercially. The last two set more slowly and developed very high strengths at early periods. These two aluminates high in alumina were later made in a pure and impure condition in larger quantities in a rotary kiln and concrete was made from the resulting ground clinker. A 1:1.5:5.5 gravel concrete developed in 24 hours as high strength as a similarly proportioned Portland cement concrete would have developed in 28 days.

Recent investigations [1] have shown that lime can combine with alumina only in the following molecular proportions: $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, $3CaO.5Al_2O_3$. These investigations also show that the tricalcium aluminate is the only aluminate present in Portland cement of normal composition and normal properties. Later these results were confirmed by work carried on at this Bureau and published as Technologic Paper No. 78.[2] In this latter paper some of the properties of the tricalcium aluminate as a cementing material are given. The present paper will present in a brief résumé these same characteristics as well as new information obtained since the first work on this compound was carried out. However, the major portion of this paper will deal with the properties of the other aluminates mentioned above, paying particular attention to the value of these as a cementing material.

Portland cement is composed of from 90 to 95 per cent of lime, silica, and alumina. The ternary system composed of these is therefore of much interest to those concerned with cementing materials, as the composition of Portland cement which will pass standard specifications [3] is confined to rather narrow limits and

[1] Rankin, "The ternary system lime-alumina-silica," Am. J. Sci., 39; January, 1915.

[2] Bates and Klein, Properties of the Calcium Silicates and Calcium Aluminates Occurring in Normal Portland Cement, B. S. Tech. Paper, No. 78.

[3] U. S. Government Specification for Portland Cement, B. S. Circular No. 33. American Society for Testing Materials, Standard Specifications and Tests for Portland Cement, serial designation C 9–17.

covers but a small area in the system when the latter is graphically presented in a triaxial diagram. The question naturally arises, as a consequence, whether any other compositions representing other areas may have cementing properties. In order to determine this point an attempt was made to produce all of the possible compounds in as pure a state as possible. It was not possible to produce all of them of the desired purity and in the quantity necessary to determine their hydraulic properties, on account of the fact that some dissociate at temperatures near their melting points. It was not feasible to prepare these latter in large quantities by crystallizing them from a glass of their composition at a temperature below their melting point. However, the entire ternary system was covered by burning of batches having compositions very close to those of all the different possible compounds, which are:

$CaO.SiO_2$	$3CaO.Al_2O_3$	$Al_2O_3.SiO_2$	$CaO.Al_2O_3.2SiO_2$
$3CaO.SiO_2$	$5CaO.3Al_2O_3$		$2CaO.Al_2O_3.SiO_2$
$2CaO.SiO_2$	$CaO.Al_2O_3$		$3CaO.Al_2O_3.SiO_2$
	$3CaO.5Al_2O_3$		

Some of these exist in two or more forms.

When the burned clinker was ground and gaged with water, it was found that of the above compounds only the α and β forms of the $2CaO.SiO_2$, $3CaO.SiO_2$, and all of the calcium aluminates had such properties as might justify their being called hydraulic cements. However, it is questionable if the two aluminates higher in lime should rightly be considered as having hydraulic properties, as their reaction with water is so energetic and accompanied by such an evolution of heat that a large excess of water is required in gaging. This produces an open porous mass which reduces its resistance to the further action of water if placed therein. They therefore show a decrease in strength when aged under these conditions. Consequently, as hydraulic cements should not show decreasing strength or slow disintegration under such conditions, the $5CaO.3Al_2O_3$ and more particularly the $3CaO.Al_2O_3$, can not properly be called hydraulic cementing materials. It was not thought advisable to make large quantities of these two aluminates on account of these properties. However, those high in alumina—$CaO.Al_2O_3$ and $3CaO.5Al_2O_3$—showed such surprising strength, especially at early ages, that it was thought desirable to make them in larger quantities and also with varying amounts of the three impurities—silica, iron oxide, and magnesia—which generally accompany lime and alumina. When the larger quan-

tities of cement were desired, they were burned in a 2 by 20 foot rotary kiln, the whole process of manufacture in general being similar to that used in producing Portland cement.

The data herewith presented are not the first to be obtained with compounds of this type. Spackman [4] has contributed considerably to the subject, but published nothing showing what compounds were actually present in the cements he used. He furthermore made no concrete test pieces. A rather extended discussion of the aluminates took place following a paper by Killig,[5] at the 1913 meeting of the German Portland Cement Manufacturers' Association. No further work was apparently done until this presented herewith, although, according to Conwell,[6] the La Farge cement works in France produced a high calcium aluminate cement ("artillery cement") for gun foundations during the late war. Endell [7] presented a paper before the 1919 meeting of the German Portland Cement Manufacturers' Association giving results obtained with cements having compositions very similar to the impure aluminates used in this investigation. He also determined the hydraulic properties of all the compounds in the $CaO.Al_2O_3.SiO_2$ system, and concludes that only the orthosilicate of lime, the monaluminate of lime, and the 3:5 calcium aluminate form true cements.

Tricalcium Aluminate $3CaO.Al_2O_3$.—When lime and alumina in the molecular proportions of three of the former to one of the latter are heated together at a temperature much beyond 1350° C, there is not produced the compound $3CaO.Al_2O_3$, but a mixture of $5CaO.3Al_2O_3$ and CaO. The presence of the latter can be readily shown by the petrographic microscope, but not by the physical properties of the ground burned material, as these are very similar to those of ground $3CaO.Al_2O_3$. It may be stated that if the burned mass shows signs of fusion or of marked vitrification then uncombined lime is unquestionably present. This inability of the lime and alumina to combine in the ratio of 3 to 1 at high temperature is due to the fact that such a compound is unstable at its melting point (1535° C), decomposing into $5CaO.3Al_2O_3$ and CaO; this decomposition starts at a much lower temperature than the melting point. To secure the tricalcium aluminate, therefore, the

[4] Spackman, "Aluminates: their properties and possibilities in cement manufacture," Proc. Am. Soc. for Test. Mat., 10, p. 315; 1910.

[5] Killig, "Calcium aluminates and their influence on hydraulic cements," Prot. Vereins Deut. Port. Cement Fabrikanten, p. 408; 1913.

[6] Conwell, Discussion of a paper by Bates—"Cements producing such hardening concretes," Proc. Amer. Soc. for Test. Mat., 19, pt. 2, p. 440; 1919.

[7] Endell, "Cement rich in alumina," Zement, 8, pp. 319–321, 334–336, 347–350; 1919.

practice at this laboratory has been to heat the mixture of the proper composition to 1400 to 1450° C for about half an hour, cool, grind, and reburn at a temperature of 1300 to 1350° C for several hours, cool, and examine microscopically for free lime. If it is present, the burned material is reground and reburned at the lower temperature mentioned until the microscope no longer reveals free lime.

The addition of water to this freshly prepared aluminate produces a very vigorous reaction, manifesting itself almost immediately by a rapid rise in temperature until the mass steams vigorously and assumes a "flash set." This is a partial hydration and is confined largely to the exterior of the individual grains or agglomerations of these. If the kneading with water is continued after the mass has cooled somewhat, there is produced a very plastic mass. It is necessary to use initially from 40 to 45 per cent of water in order to have enough present after the steaming to permit of the continued kneading. When this action is carried on vigorously for several minutes, there is produced a smooth plastic mass, which, with still further working but with no further addition of water, becomes so fluid that it will not permit of the making of a pat. It has not been possible to produce a smooth pat free from large agglomerations of unaffected aluminate by the use of less water than the amounts given above.

The partially hydrated aluminate, after the continued kneading following the flash setting, acquires a kind of final set. This may take place in an hour or may require two or three days, depending upon how hot the mass is after the kneading. If it still remains very warm, the heat seems to accelerate the setting, especially by evaporation. On the other hand, if it has become cooled to about room temperature, a much longer period ensues before setting takes place.

The test pieces after final setting has taken place are still comparatively soft and can be indented with the finger nail. Any surface not exposed to the atmosphere during setting is perceptibly softer than one which has been so exposed. If the kneading following the flash set has not been thorough enough to completely break up all agglomerations and make a smooth paste, the "steaming test" will disintegrate the test pieces.

The effects of the addition of SO_3 in the form of plaster of Paris to the aluminate alone and to the latter when it contained 2 per cent of hydrated lime are shown in Table 1.

TABLE 1.—Time of Set of Tricalcium Aluminate

[All samples gave a flash set. All results shown were obtained by thorough kneading of the set material]

Percentage composition				Penetration, Vicat plunger	Initial set		Final set	
$3CaOAl_2O_3$	Gypsum	$Ca(OH)_2$	H_2O		Vicat	Gilmore	Vicat	Gilmore
					H. m.	H. m.	H. m.	H. m.
100	.....	.....	40	None.....	(a)	(a)	(a)	(a)
100	.....	.....	45	.....do.....	(a)	(a)	(a)	(a)
97.5	2.5	.....	41	.....do.....	(a)	(a)	(a)	(a)
97.5	2.5	.....	45	.....do.....	(a)	(a)	(a)	(a)
95.5	2.5	2.0	41	.....do.....	(a)	(a)	(a)	(a)
95.0	5.0	.....	41	9 mm.....	0 07	0 14	5 20	(b)
93.0	5.0	2.0	41	To bottom.....	0 23	0 43	1 30	4 30
93.0	5.0	2.0	37	11 mm.....	0 21	0 38	1 15	1 15
90.0	10.0	.....	41	.....do.....	0 23	0 52	0 50	1 00
88.0	10.0	2.0	41	To bottom.....	0 30	1 15	0 55	1 20
88.0	10.0	2.0	37	15 mm.....	0 25	1 10	0 55	1 15
85.0	15.0	.....	41	To bottom.....	1 10	3 50	6 30	6 30
85.0	15.0	.....	37	15 mm.....	0 40	3 00	6 30	6 30
83.0	15.0	2.0	37	20 mm.....	0 25	1 50	6 00	7 30
83.0	15.0	2.0	34	6 mm.....	0 18	1 45	(b)	(b)
80.0	20.0	.....	41	To bottom.....	1 00	3 50	(b)	(b)
80.0	20.0	.....	37	15 mm.....	0 45	3 50	(b)	(b)
78.0	20.0	.....	37	25 mm.....	0 55	3 50	(b)	(b)
78.0	20.0	2.0	34	7 mm.....	0 50	3 50	(b)	(b)

[a] Violent steaming prevented continuous kneading. (See text.)
[b] Set between 7¼ and 22 hours.

It is seen from the table that 2 per cent of hydrated lime, or 2½ per cent of plaster alone or in the presence of 2 per cent of the hydrate, changed the setting properties but little. There resulted in all cases a flash set followed by a violent steaming which necessitated the stopping of the kneading for a time. Later the mass could be kneaded into a smooth plastic condition which, as stated above, gave a final set of from 1 hour to 2 or 3 days. Five per cent of plaster retarded the steaming sufficiently to permit of the making of test pieces. These gave off steam at the time of initial set, which varied considerably with the Vicat or Gilmore test pieces, on account of the different volumes of the test pieces. Five per cent of plaster in the presence of 2 per cent of hydrated lime produced a much more marked retardation of the initial set, but accompanied as before by an evolution of steam. Increasing amounts of plaster produced increased retardation of the initial and usually also of the final set. Steaming occurred at about the time of final set when 10 or 15 per cent plaster was used. Lime hydrate in the presence of these larger amounts of gypsum decreased the amounts of water required for gaging. It should be particularly emphasized that flash setting occurred in all cases, and the results given were obtained by thorough kneading after the appearance of this phenomenon.

The Vicat test pieces placed in water at the end of 24 hours disintegrated in the course of a few hours. If allowed to harden for several days they did not disintegrate rapidly, but in the course of several months they checked on the surface and increased very much in volume.

On account of these several properties and the fact that previous work of the Bureau showed that this aluminate did nor develop any strength as a bonding material, no specimens to determine the strength were made in this investigation. The tricalcium aluminate is apparently not a true hydraulic cement, and the heat evolved in gaging with water and the later increase in volume do not permit of its wide practical application.

The question may arise as to why Portland cement, which contains approximately 20 per cent of this compound, does not show more of the characteristics of the latter. The answer is to be sought perhaps in the condition in which the tricalcium aluminate occurs in the cement clinker as revealed by examining through the microscope a thin section of clinker. It is then seen that in normal clinker the constituents do not exist with a well-defined outline nor separated into well-defined crystals. This is shown in Fig. 1, photomicrographs made by transmitting light through a thin section of a typical Portland cement clinker. The dicalcium silicate, the major constituent, exists in fairly large grains which blend off into a more or less homogeneous boundary containing the tricalcium silicate, tricalcium aluminate, and the dark-colored iron compounds. Although in a clinker burned at a high temperature for a comparatively long time and having a high silicate content, the tricalcium silicate may exist in large, well-defined crystals, such a clinker is an exceptional one. It can be readily seen that in grinding normal clinker, the grains will not be separated grains of any one constituent, as they would be in a mechanical mixture, but even the finest ground particles may be composed of all the constituents. Therefore the activity will be reduced a certain degree by the inability of the water to reach all of its surface.

The activity of the aluminate will be furthermore masked by the presence of the dicalcium silicate which is present in amounts about two and a half times as great. This is relatively very inactive toward water, shows a setting time of several days, and does not evolve heat to a perceptible degree. The activity is furthermore modified by the presence of the gypsum added during the grinding of the clinker. This latter is added usually to an

amount equal to 3 per cent of the weight of the clinker, which is equivalent to about 15 per cent of the aluminate. Also on adding water to ground cement, the tricalcium silicate starts to hydrate by splitting off lime. The effects of both lime and gypsum on reducing the activity of the pure aluminate have been discussed above, and these in connection with the condition in which the aluminate exists in clinker explain why its properties when in the pure condition are not distinctly manifested when in Portland cement clinker.

$5CaO.3Al_2O_3$.—This aluminate can be prepared in the pure condition without any great difficulty, as it shows no tendency to decompose at temperatures approaching its melting point. Its activity toward water is distinctly less than that shown by the tricalcium aluminate. By the use of about 10 per cent more water (in terms of the cement) than is used in gaging Portland cement it is possible to knead thoroughly the aluminate with water without the appearance of any flash set. Initial set occurs in from 3 to 5 minutes after molding, and final set occurs in from 15 to 30 minutes, the latter being accompanied by a marked evolution of heat. Plaster of Paris retarded the initial set to a very slight degree, but the final set was retarded about one hour.

This compound attained considerable strength both in the neat condition and in a 1:3 mortar. Thus the average neat tensile strength of two burnings at 7 days was 275 pounds per square inch, and at 28 days 311 pounds; the neat compressive strength was 3090 pounds and 3670 pounds at 7 and 28 days, respectively. The tensile strength of the 1:3 standard sand mortars was relatively much higher, being 261 pounds per square inch at 7 days and 264 pounds at 28 days. The mortar strength was also high in compression, being 1750 pounds at 7 days and 1300 pounds at 28 days. The addition of plaster produced a 50 to 100 per cent increase in strength. This was more marked at 28 days, so that the slight increases in strength (or retrogressions in some cases) between the 7 and 28 day periods were very much enlarged.

The hydration of this aluminate consists in the formation of hydrated tricalcium aluminate and hydrated alumina. The hydration of all of the aluminates consists of this same reaction, all of the alumina in excess of that required for the ratio of three lime to one of alumina forming a gelatinous mass of hydrated alumina when the aluminate is completely hydrated. As this is the molecular ratio of the components of tricalcium aluminate, of necessity no alumina is split off from the latter and the sole

product of its hydration is tricalcium aluminate having a varying number of molecules of water present, depending upon whether it exists in a colloidal or crystalline form.[8]

This aluminate was not produced in large enough amounts to permit of the making of concrete specimens on account of its rapid setting qualities. Simultaneous work with the two other aluminates of higher alumina content showed that they did not possess this property of rapid set but did develop very high strengths. Therefore further work on the $5CaO.3Al_2O_3$ compound was discontinued, and the remainder of the investigation was devoted to $CaO.Al_2O_3$ and $3CaO.5Al_2O_3$, both in the pure and impure condition.

$CaO.Al_2O_3$ and $3CaO.5Al_2O_3$.—As the preliminary work with these two aluminates showed that they had such properties as would recommend them for use as hydraulic cements, it was thought desirable to make burnings of such a size as would give sufficient material to permit of making concrete specimens to be broken at late ages as well as the usual small mortar test pieces. Eight burns in all were made in the 2 by 20-foot rotary cement kiln of this Bureau. In these the alumina content varied from 30.5 to 74.1 per cent. The constituents, other than lime and alumina, in three of the burns were as low as it was possible to have them without using chemically pure lime and alumina. In these three particular burns, where the desire was to produce either $CaO.Al_2O_3$ or $3CaO.5Al_2O_3$ in as pure condition as possible, the total amount of silica, iron oxide, and magnesia did not exceed 1.89 per cent in the clinker. Varying amounts of these three impurities were introduced purposely in the other five burns to determine how the properties of the pure aluminate would be affected by these. The minimum amount of silica was 9.41 per cent, the maximum amount 17.38 per cent; the minimum amount of iron oxide was 1.85 per cent and the maximum 3.10 per cent; and the magnesia had 1.04 and 3.66 per cent as the minimum and maximum percentages. These limits were used because it was believed that they would represent the amounts of impurities that might be encountered in using commercially available sources of raw material.

The pure aluminates were made from a limestone low in all impurities, and calcined alumina. The former came from a large deposit of a very pure limestone in York County, Pa., and the latter was purchased from a dealer in certain ceramic supplies and

[8] Klein and Phillips, Hydration of Portland Cement, B. S. Tech. Paper No. 43.

was made from either bauxite or cryolite. While limestones comparatively low in impurities are widely scattered throughout the country, such is not the case with respect to alumina. In this case, were it desired to produce the lime aluminate on a commercial scale, recourse to bauxite or to highly aluminous clays as a scource would be necessary. These would be used to the maximum allowable amount, as determined by the effects of the impurities present, and any deficiency in alumina would be made up by adding such a material as the above-mentioned calcined alumina, or an alumina obtained as a by-product in some of the recently established processes of obtaining potash from alunite or felspar. The high cost of a pure alumina would totally preclude its use as the sole source of the alumina in the aluminate.

The impure aluminates referred to in this investigation (see Table 2) as Nos. 3, 4, and 5 were made of a raw batch composed of the above-mentioned limestone, kaolin, alumina, and iron oxide. The raw batch of No. 6 contained in addition to these some flint, while that of No. 7 contained all of these but the kaolin, which was partially replaced by bauxite.

The composition of the raw batches, the analyses of the clinker, and the temperature at which the burnings were made are given in Table 2. The raw batch was ground to such a fineness that at least 85 per cent passed a 200-mesh sieve. The alumina and flint, as received, were of a fineness of more than 90 per cent through the same sieve. The temperatures of burning given in the table are the average of temperature readings taken every 15 minutes throughout the burns, which usually required from 4 to 5 hours. The pyrometer used was of the Holborn-Kurlbaum type, and the readings are probably accurate to $\pm 15°$.

TABLE 2.—The Raw Composition, Analyses, and Temperatures of Burning of the Clinker

Cement No.	1	2	3	4	5	6	7	8
Raw composition:								
Limestone.....pounds..	350.0	350.0	280.0	341.5	315.0	396.0	325.0	255.0
Alumina.....do....	360.5	360.5	238.0	172.5	108.0	94.5	190.0	450.0
Kaolin.....do....	.....	.....	105.0	97.5	180.0	93.0	.....	.....
Iron oxide.....do....	.....	.....	10.5	9.5	9.0	5.0	5.0	.....
Bauxite.....do....	.....	.....	.....	.....	.....	.....	160.0	.....
Potters flint.....do....	.....	.....	.....	.....	.....	37.5	.....	.....
Clinker analyses:								
SiO_2.....	0.44	0.76	9.41	10.48	17.23	17.38	11.33	.68
Al_2O_3.....	62.31	61.25	55.09	46.71	39.96	30.52	47.66	74.11
Fe_2O_3.....	.51	.60	2.04	2.13	2.57	1.85	3.10	.40
CaO.....	36.69	36.32	30.73	39.79	38.84	46.72	34.87	23.82
MgO.....	.36	.48	2.95	1.04	1.29	2.27	3.66	.81
Ig. loss.....	.07	.50	.08	.32	.14	.78	.17	.38
	100.88	99.91	100.30	100.47	100.03	100.52	100.19	100.20
Temperature of burning, degrees centigrade.....	1460	1480	1490	1380	1455	1360	1445	1500

When this investigation was started, the work of Rankin on the lime-silica-alumina system had not been published, and consequently the temperatures which any burn would require were known only in a very general way. However, in all cases the burnings were made at the lowest temperature at which the clinker would appear to show the start of vitrification. When such clinker appeared the temperature was allowed to vary as little as possible. It must be stated, however, that generally the impure aluminates were burned at too high a temperature, and the clinker was harder than desired. This was due to the fact that these exhibited a very narrow range of temperature between that at which they were underburned (showing a tendency to "dust") and that at which they formed "balls" or "logs" or even melted in the kiln. This is true of burns Nos. 5 and 6, and especially true of the latter, which unless quenched in water on falling from the kiln dusted rapidly and completely. Quenching, however, was not followed, but the clinker was allowed to cool in the air.

It can be noted from the data that the temperatures of burning are not much higher than those used in the production of Portland cement. Seventy-five samples of "raw mixes" received from various manufacturers of Portland cement in the United States gave an average clinkering temperature of 1435° C. This was the average lowest temperature at which the clinker from these raw mixes showed microscopically the absence of free lime. The time of burning of these was the same, as stated by the manufacturers furnishing them, as that required to produce the cement commercially. Furthermore, while 1435° C was the average temperature of burning of the commercial raw mixes, yet some required a temperature in excess of 1500° C. The temperatures used in producing these aluminates are not therefore in excess of those used in commercial rotary kiln practice.

One point in connection with the burning should be particularly emphasized, and that relates to the nature of any underburned products. Underburning to a certain degree in the case of Portland cement produces what is called "unsound" cement. This is cement which, when gaged with water and the hardening accelerated at the end of 24 hours by heating at 100° C in an atmosphere of steam, shows such permanent expansion that the test piece warps, cracks, or softens. This expansion is due especially to the presence of too much uncombined lime.[9] In these

[9] It is not within the province of this paper to enter into a detailed discussion of all the phases of the "unsoundness" of Portland cement or how it is fully caused. The above statement covers in a broad but brief way the cause and manifestation of these phenomena, but does not go into the details of showing how a certain amount of uncombined lime in one clinker may exhibit unsoundness and the same amount in another not show this condition.

aluminates, particularly Nos. 1, 2, and 8, the total amount of lime is very low, when compared with the amount in Portland cement, and the alumina correspondingly high. The lime will have all combined during the burning, and any uncombined material will be alumina. This latter does not react with water, as does lime, and therefore will not show the expansion and disruption shown by the free lime of Portland cement. Underburning of the impure aluminates is shown particularly by the dusting of the clinker. This is due to the fact that the burning has not been conducted at a sufficiently high temperature (or for a sufficiently long period at a lower temperature) to produce the β form of the orthosilicate in a stable state. In cooling it reverts to the γ form of the same silicate accompanied by an increase in volume of about 10 per cent. Even in the impure aluminates, the relative amounts of lime are so low that at low temperatures it is all combined with silica or alumina and no products are present which manifest excessive expansion on hydrating. Consequently it is not possible to produce unsound cement with materials approaching the composition used in this investigation without the use of temperatures far lower than those given in Table 2.

The addition of the impurities tended to cause a lowering of the temperatures required for satisfactory burning. This is in accordance with the rule that generally the introduction of a third compound into a binary system produces a lowering of softening points as the ternary field is entered. Cement No. 3 is no exception to this statement, notwithstanding the fact that it was burned at an average temperature of 10° C. higher than No. 2. The clinker produced in the former case was decidedly harder than the latter. To those engaged in the manufacture of Portland cement, the fact that an increase of lime produces a lowering of clinkering temperature may seem strange. But the work of Rankin, previously cited, shows that the trend of the softening points of lime-alumina mixtures is downward from the melting point of pure alumina at 2050° C. to the melting point of the eutectic between $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ (50 per cent lime and 50 per cent alumina) at 1395° C, and then upward to the melting point of pure lime at 2570° C. The compositions of the aluminates here considered all lie between $5CaO.3Al_2O_3$ and Al_2O_3, hence an increase in lime will produce a lowering of the clinkering temperatures except in the neighborhood of eutectic points. These latter, however, are characterized in the binary system by a slight temperature change for marked changes in composition,

and consequently would not be very pronounced in considering trends of temperature changes. Fig. 2, which shows the location of the compositions under investigation in the ternary system, also shows the melting temperatures of the compounds of lime and alumina and their eutectics according to Rankin. This should materially assist in understanding the changes in clinkering temperatures produced by changes in composition. This applies only to compositions containing lime, silica, and alumina, but as stated

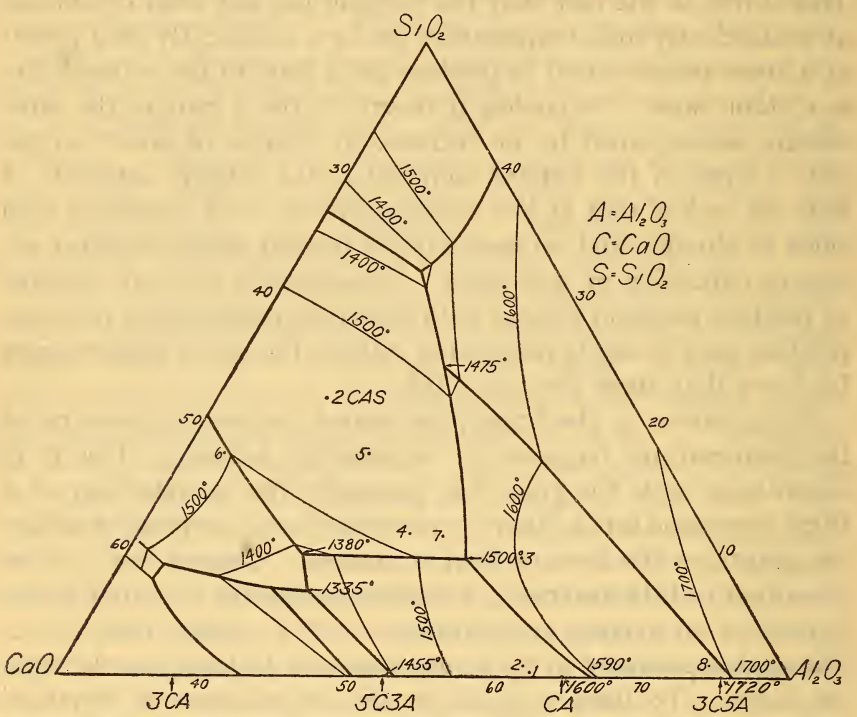


FIG. 2.—*Projection of a portion of the ternary system $CaO.Al_2O_3.SiO_2$ showing the location of the cements under investigation, with isotherms (light lines), boundaries (heavy lines) between some of the fields, and melting temperatures of some of the compounds*

before, the introduction of impurities tends to lower the clinkering temperatures.

The appearance of the clinker of the several burns was of course decidedly different from that of Portland cement. That from Nos. 1, 2, and 8 was whiter than the clinker of white Portland cement and was composed of soft nodules about 1 inch or less in diameter. No. 6 gave a gray slaglike clinker which rapidly dusted to a light-gray dust. No. 5 also was of a gray color, but the exterior of the nodules was rough like Portland-cement clinker,

while the interior was more completely vitrified. Dusting of this clinker was pronounced but not excessive. No. 4 gave a yellow slaglike clinker. Nos. 3 and 7 gave a hard clinker of about the size obtained with Portland cement, black and well vitrified on the interior, but yellow to reddish brown on the exterior. The black glistening appearance of the exterior of Portland cement clinker was at all times lacking.

All clinker was examined petrographically to determine the character and relative amounts of the constituents. These data are given in Table 3. Here the constituents are arranged in order of the amounts present in each particular case. This table should, however, be studied in connection with Table 2 showing the chemical analyses, otherwise it is likely that the proper conception will not be formed of the relative amounts of some of the constituents, as the orthosilicate or the ternary compounds, which are present. Thus while Nos. 3 and 8 show the same constituents in the same order, manifestly No. 3 must contain much more of the ternary compound than No. 8, as the latter contains but 0.68 per cent silica while the former contains 9.41 per cent, and, furthermore, in both cases all of the silica is combined as $2CaO.Al_2O_3.SiO_2$.

TABLE 3.—The Constituents of the Clinker

[C=CaO; A=Al_2O_3; S=S_1O_2]

Cement No.....	1	2	3	4	5	6	7	8
Major constituent.....	3C5A	CA	CA	2CAS	2CAS	2CS	2CAS	CA
	CA	5C3A	3C5A	CA	CA	5C3A	CA	3C5A
Minor constituent.....	2CS	2CS	2CAS	2CS	2CS	CA	2CS	2CAS

The clinker of Nos. 1 and 8 was soft and very fine grained. The petrographic examination of the former was especially difficult, but judging largely from the indices of refraction it was composed mainly of $CaO.Al_2O_3$. This same compound was rather well developed in No. 8, but the main constituent in this case was $3CaO.5Al_2O_3$ existing in poorly defined grains. No. 3 gave a clinker with much better defined crystals, and the constituents noted could be identified comparatively readily. The other burns yielded clinker in which some of the constituents were very well crystallized. These are shown in Fig. 3. These crystalline compounds are either $3CaO.5Al_2O_3$ or the ternary compound $2CaO.Al_2O_3.SiO_2$. Their optical properties are such that they can not be satisfactorily differentiated in thin sections. However, the

immersion method of examination showed that Nos. 5 and 7 contained no $3CaO.5Al_2O_3$. Hence in these two cases the crystals are those of the ternary compound. These sections are typical of the burns containing the impurities. However, the crystalline portions do not extend throughout the mass, but are segregated in certain portions. In this respect they resemble crystalline Portland-cement clinker where crystals in even well crystallized clinker occupy but a comparatively small percentage of the mass and are invariably localized.

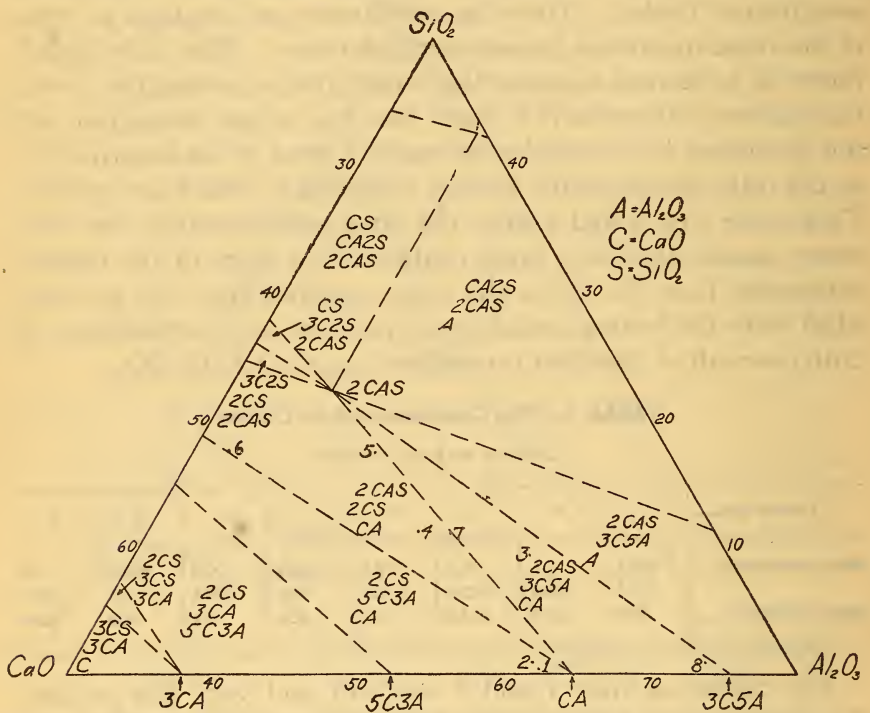


FIG. 4.—*Showing the location of the cements under investigation in the ternary system and the final products of crystallization of solutions of* $Al_2O_3.SiO_2.CaO$

There is shown in Fig. 4 the position of these cements in the ternary system. (In locating these the iron oxide has been considered as alumina and the magnesia as lime.) This figure shows but that portion of the entire system which concerns this investigation. The special reason for its presentation here is to show what the final products of crystallization would be according to Rankin, and to enable one to compare them with the products actually found as shown in Table 3. Any composition of the oxides which lies within any of the areas partly closed by dotted lines would, when equilibrium has been reached, contain either

a

b

FIG. 3.—*Examples of crystallization in the aluminate cements; (a) from a thin section of cement 3, × 50; (b) from a thin section of cement 5, × 90*

those compounds indicated as occurring within these areas or else a compound indicated as occurring in one of the adjoining areas. These areas are furthermore triangles (as would be seen if the whole ternary system were reproduced) and are formed by lines drawn from points representing compositions of either binary or ternary compounds. The compounds indicated as appearing in any triangle are those whose compositions are located at one of the apices.

A comparison such as indicated above reveals that notwithstanding the fact that the burning at the recorded temperature was but for a comparatively brief period, yet the constituents present were those which would result if the burning had continued until equilibrium would have been reached. Attention should be called to the fact that the petrographic examinations of the clinker were made before the work of Rankin was at hand, and hence it is very gratifying to note how the work of the latter corroborated the above examinations.

The clinker, without any storage, was crushed and ground to the fineness shown in Table 4. After crushing, but before grinding in ball mills, the clinker was divided into two portions. The one portion was ground with 3 per cent of plaster of Paris, the other was ground with no addition of foreign materials. It was soon found that the cements containing the plaster were not developing as high a strength in concrete as those free of this material. Consequently the concrete specimens in the later burns were made mostly from unplastered cements. In Table 4 and in the remainder of this paper the cements containing the plaster are referred to by the proper numeral and the letter "P"; when referring to the unplastered cements, the numeral alone is used.

TABLE 4.—Fineness of the Cement

Cement No.	Per cent passing—		Cement No.	Per cent passing—	
	100-mesh sieve	200-mesh sieve		100-mesh sieve	200 mesh sieve
1	98.8	83.2	4P[a]	97.0	78.0
1P[a]	99.2	82.8	5	97.6	80.2
2	98.0	80.0	5P[a]	97.8	79.4
2P[a]	99.6	82.2	6	93.0	76.4
3	99.0	81.2	7	98.2	79.8
3P[a]	98.8	81.8	8	99.7	86.6
4	96.8	78.0			

[a] Indicates the addition of plaster.

In Table 5 is presented the time of set of both the plastered and the unplastered cements as determined by both the Gilmore and Vicat needles. The setting time is either too rapid or too slow when compared with the time of set required for Portland cements of standard specification. These latter require an initial set of not less than 60 minutes when the Gilmore needle is used, not less than 45 minutes when the Vicat needle is used, and a final set within 10 hours as determined by either needle. But while too early an initial set may interfere in the practical use of a cement, nothing can be said against a final set in excess of 10 hours if the 24-hour strengths are high enough. Such is the case with the three slow-setting cements of this group. While they have not attained a final set within 8 hours, they have in all three cases in 24 hours a tensile strength as a 1:3 standard sand mortar in excess of that required of Portland in 7 days, and in two of the three cases a strength in excess of that required at 28 days.

TABLE 5.—Consistency and Time of Initial and Final Sets

Cement No.	Initial		Final		Consistency (per cent water)
	Gilmore	Vicat	Gilmore	Vicat	
	H. m.	H. m.	H. m.	H. m.	
1	0 55	0 25	4 45	2 10	27.0
1P	0 50	0 15	4 55	2 30	27.0
2	0 30	0 10	2 00	0 50	25.0
2P	0 40	0 05	3 50	0 50	25.0
3	6 25	5 15	(a) (a)	7 05	21.0
3P	0 25	0 20	6 20	3 25	21.5
4	0 35	0 10	3 30	1 15	22.0
4P	0 10	0 03	1 40	0 25	20.0
5	0 40	0 15	4 45	3 15	21.5
5P	0 15	0 15	3 00	0 30	21.5
6	0 07	0 02	0 45	0 12	29.0
6P	Flash	Flash	Flash	Flash	30.0
7	6 00	3 45	(a) (a)	(a) (a)	19.0
7P	0 35	0 20	4 30	2 30	19.0
8	7 00	3 30	(a) (a)	(a) (a)	26.0
8P	1 05	0 20	4 00	2 45	26.0

[a] Final set occurred between 8 and 16 hours after mixing.

When the time of set is studied in connection with the constitution and composition, it is further evident that the alumina in the cements high in alumina is combined to form an aluminate in which the ratio of lime to alumina is low. This follows from the fact that these ($CaO.Al_2O_3$ and $3CaO.5Al_2O_3$) react with water

much more slowly than the others high in lime. The other constituents present, $2CaO.SiO_2$ and $2CaO.Al_2O_3.SiO_2$, react very slowly also. It is hardly possible to remove test pieces made of the former from molds within 2 weeks. The latter have not been noted to acquire set at all. In all cases under consideration the setting phenomena noted have been due therefore to the properties of the aluminates or to these properties as modified by plaster. The latter has invariably produced a marked acceleration of both initial and final set. No very satisfactory explanation can be offered in regard to this phenomenon. It has been stated before that the normal hydration of these aluminates consists in the formation of hydrated tri calcium aluminate and hydrated alumina, both separating at early periods in a colloidal form. It is possible that in the presence of the plaster the solubility of the aluminate is increased to a greater degree, and within the same period a greater amount of the colloidal material will separate out, than if it had not been present. This more rapid solution and coagulation would produce a more rapid set.

For determining the strength-developing properties of these aluminous cements, the customary neat and 1:3 standard sand briquettes were made, as well as 2-inch compression cubes of the standard sand mortars and 6 by 12 inch gravel concrete cylinders of several proportions. The majority of these test pieces were made from both the material containing plaster and that not containing the latter. This is particularly true of the small specimens which were made before the concrete specimens, and which showed that the presence of plaster reduced the strength.

The small specimens were generally stored in water after the first 24 hours in the damp closet and the concrete specimens were stored continuously in the latter. However, other work had shown the marked increase in strength if the test pieces were stored in the water for one-quarter of their age and then stored in the air of the laboratory. Hence for certain periods this kind of storage was used in addition to the ordinary storage. This "combined storage" method was used also for the concretes tested at one year, but the storage in the damp closet was somewhat longer, having been six months for the test pieces made from cements 1 to 5, inclusive, and four months for those from 6, 7, and 8.

The data obtained from breaking these test pieces are presented in Tables 6 to 9, inclusive.

TABLE 6.—Tensile Strength of Neat Specimens in Pounds per Square Inch

[C S=Stored for one-fourth of period in water and the remainder in the air of laboratory. W P=Cement contained no plaster. P=Cement contained 3 per cent plaster. B=Broke by handling while placing in the machine]

Cement No.	1	2	3[a]	4	5	6	7	8
Tested at 24 hours: Stored in water—								
W P	455	590	.....	505	320	385	630	345
P	375	315	.....	585	300	385	385	405
Tested at 7 days: Stored in water—								
W P	220	100	.....	715	490	265	955	825
P	790	510	.....	880	475	215	500	290
Tested at 28 days:								
Stored in water—								
W P	130	150	.....	750	505	503	1020	535
P	810	845	.....	955	490	500	475	210
Stored in C S—								
W P	315	385	.....	910	595	280	880	975
P	525	470	.....	815	725	370	680	680
Tested at 90 days: Stored in water—								
W P	200	200	.....	880	545	495	1105	130
P	680	635	.....	725	545	480	905	28
Tested at 26 weeks:								
Stored in water—								
W P	260	120	.....	910	610	530	790	160
P	135	145	.....	820	515	320	470	175
Stored in C S—								
W P	85	50	.....	510	580	360	840	620
P	475	570	.....	500	580	260	885	190
Tested at 1 year: Stored in water—								
W P	185	145	.....	960	665	445	700	130
P	135	165	.....	630	500	415	840	125
Tested at 3 years: Stored in water—								
W P	225	255	.....	1100	640	500	525	B
P	200	185	.....	440	545	375	530	B

[a] No neat test piece made.

TABLE 7.—Tensile Strength of 1:3 Standard Mortars in Pounds per Square Inch (Average of 3 test pieces)

[C S=Stored for one-fourth of period in water and remainder of period in air. P=Plaster added to the cement. W P=No plaster added to the cement]

Cement No.	1	2	3	4	5	6	7	8
Tested at 24 hours: Stored in water—								
W P	370	275	270	415	155	220	345	330
P	380	295	195	355	155	175	250	370
Tested at 7 days: Stored in water—								
W P	403	385	385	280	170	175	295	690
P	360	305	360	335	155	115	225	390
Tested at 28 days:								
Stored in water—								
W P	435	320	525	335	170	280	290	540
P	310	595	345	310	175	100	295	280
Stored in C S—								
W P	730	305	615	345	365	405	560	830
P	720	570	585	415	370	285	515	530
Tested at 90 days: Stored in water—								
W P	440	395	560	375	225	285	350	770
P	465	480	390	355	172	135	370	195
Tested at 26 weeks:								
Stored in water—								
W P	525	390	575	500	300	245	385	590
P	530	375	480	427	163	170	360	380
Stored in C S—								
W P	595	500	900	400	535	605	575	960
P	525	445	665	555	540	315	595	425
Tested at 1 year: Stored in water—								
W P	525	425	610	435	320	295	390	700
P	550	470	490	440	185	140	330	460
Tested at 3 years: Stored in water—								
W P	715	605	560	545	350	335	425	615
P	555	605	335	580	260	155	200	460

TABLE 8.—Compressive Strength of 1:3 Standard Sand Mortars in Pounds per Square Inch (Average of 3 Test Pieces)

[C S=Stored for one-fourth of period in water and the remainder in the air of the laboratory. W P=Cement contained no plaster. P=Cement contained 3 per cent plaster]

Cement No.	1	2	3	4	5	6	7	8
Tested at 24 hours: Stored in water—								
W P	3570	4260	2240	4410	1035	1340	2165	2860
P	2860	3050	1830	3380	1060	1060	1870	2710
Tested at 7 days: Stored in water—								
W P	5945	4760	4940	4880	1400	1260	5140	8610
P	2955	4090	2450	2200	1180	940	1720	4290
Tested at 28 days:								
Stored in water—								
W P	3765	3945	6475	5285	1820	1425	3930	7845
P	2790	3535	2540	2965	1160	790	1415	3680
Stored in C S—								
W P	6815	7625	8000	6400	2875	3130	7085	10690
P	4005	5515	4655	5140	2665	2315	3610	7415
Tested at 90 days: Stored in water—								
W P	3945	4735	7180	4565	2070	1680	5205	8260
P	3015	4630	3210	2495	1465	925	2630	4745
Tested at 26 weeks:								
Stored in water—								
W P	5330	4570	7760	3470	2900	1895	3605	6380
P	3860	4850	4630	2270	2200	1475	3080	4605
Stored in C S—								
W P	6015	5290	11050	3480	3845	4345	6090	8045
P	4945	5470	7100	4920	3540	3055	5430	7475
Tested at 1 year: Stored in water—								
W P	3045	4430	5315	3200	2410	2310	5225	8945
P	2850	3580	3015	2355	1720	685	2010	4260
Tested at 3 years: Stored in water—								
W P	3410	4960	5910	3185	3400	2330	3055	8640
P	2815	4110	3115	2730	2785	1345	2480	3285

TABLE 9.—Compressive Strength of 1:1.5:4.5 and 1:3:9 Gravel Concrete in Pounds per Square Inch (Average of 3 Test Pieces)

Cement No.	1[a]	2	3	4	5	6	7	8
Tested at 24 hours: Proportions—								
1 : 6	2825	3000	Soft.	3145	310	840	1475	2930
1 : 12	.....	.....	.....	880	Soft.	275	455	890
1 : 12P	.....	1500	.....	1630	.....	315	375	470
Tested at 7 days: Porportions—								
1 : 6	3270	4150	2175	3570	885	765	4135	6010
1 : 12	.....	.....	.....	1005	225	275	1405	2270
1 : 12P	.....	1590	.....	1435	.....	400	675	1480
Tested at 28 days: Proportions—								
1 : 6	3310	4740	3680	3370	1250	990	4625	7060
1 : 12	.....	.....	.....	1000	365	305	1500	3415
1 : 12P	.....	1890	.....	1415	.....	410	645	1740
Tested at 90 days: Proportions—								
1 : 6	4150	2480	3900	2930	1050	1260	4640	7050
1 : 12	.....	.....	.....	875	390	400	1600	3980
1 : 12P	.....	1580	.....	1280	.....	700	800	1760
Tested at 26 weeks: Proportions—								
1 : 6	4180	1760	4525	2565	1270	1515	4450	7610
1 : 12	.....	.....	.....	800	550	470	1580	3910
1 : 12P	.....	1580	.....	1385	.....	570	600	1700
Tested at 1 year: Proportions—								
1 : 6	3310	1760	4135	2565	1460	1440	4650	6720
1 : 6[b]	5540	2360	5660	3280	2110	2035	5300	8220
1 : 12	.....	.....	.....	860	570	470	1350	3930
1 : 12[b]	.....	.....	.....	1275	870	810	1815	4445
1 : 12P	.....	1530	.....	1525	.....	600	655	1470
1 : 12P[b]	.....	2250	.....	2480	.....	1055	1080	2450
Tested at 3 years: Proportions—								
1 : 6	2080	1835	4720	2415	2035	1700	3400	5675
1 : 6[b]	2230	2160	5060	3050	2005	2215	3840	7540
1 : 12	.....	.....	.....	900	875	1055	1780	2670
1 : 12[b]	.....	.....	.....	1180	910	865	1865	3915
1 : 12P	.....	1605	.....	1860	.....	865	855	1400
1 : 12P[b]	.....	1695	.....	2160	.....	1145	1080	2470

[a] Cement used in making specimens for cement 1 contained 3 per cent plaster, also all specimens in lines headed 1 : 12P were made from cement containing 3 per cent plaster. None of the other cements contained plaster.

[b] These specimens were stored first in the damp closet (for the first 6 months in the case of cements 1–5, inclusive, and 4 months for cements 6–8) and for the remainder of the period in the air of the laboratory. All other specimens were stored in the damp closet for the entire period aged.

As usual it will be seen from these that the cements do not give a neat tensile strength which seems to bear any relation to the strength which the same cement will develop as a mortar or a concrete. Such is the case generally also with Portland cement, and consequently the Government revised specifications [10] for the latter material do not recognize nor require a neat test piece. The following data (Table 10), selected from Tables 6 to 9 and showing the strength at the end of one year for certain test pieces made from the cements containing no plaster, will illustrate this.

TABLE 10.—Strengths (at the End of One Year) of Cement Test Pieces Containing no Plaster

Specimen and test	Strengths for cement No.—				
	2	4	6	7	8
	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²
Neat, tension	145	960	445	700	130
1:3 mortar, tension	425	435	295	390	700
1:3 mortar, compression	4430	3200	2410	5225	8945
1:6 concrete	1760	2965	1440	4650	6720

At the same time it can not be stated that Table 10 shows any relation between the strengths developed by the same cement in any of the four forms of test pieces used. That there should not be any relation between the tensile strength and the compressive strength is not surprising when the marked difference in the shapes of the tension and compression test pieces is considered. The former have been analyzed and discussed to a considerable degree,[11] and it has been shown that such a shaped test piece does not satisfactorily distribute the stresses applied to it during the breaking in a testing machine. This is especially true of such a rigid material as set cement, or bodies, such as mortars, containing it.

There must also be borne in mind the actual difference in the materials of which the test pieces are made. The differences in physical properties between a neat cement test piece and one made of mortar are generally conceded. There is also reason to grant a difference between a mortar and a concrete specimen. The methods of making the former are such as would produce a body differing from the latter. Thus the constituents of the mortar

[10] U. S. Government Specification for Portland Cement, B. S. Circular No. 33.

[11] J. B. Johnson, Materials of Construction, edition 4, page 435. Coker, The distribution of stresses at the minimum section of a cement briquette, paper 284, section 2, Proc. Internat. Soc. for Test. Mat.; 1912.

are kneaded and rubbed together in the mixing and usually they are in actual contact with the hand; the concrete, however, is only mixed together by various implements in the hands of the operators. In molding there is again a marked difference of procedure, the mortar being placed in the mold in relatively much smaller quantities and subjected to much more compacting. Neglecting the character of the large aggregates and the difference in the degree of hydration which takes place in the several types of specimens, it would seem that a mortar should differ both from a concrete and from a neat cement also on account of the difference in cohesive and adhesive properties developed by the different cements in setting. Thus the formation of much colloidal material alone would develop the property of the cement to bond foreign materials (fine or coarse aggregate) together (adhesive strength) as opposed to the marked formation of crystalline material replacing some colloidal material. This latter would bond together the hydrated cement itself, as in the neat specimens (cohesive strength), but would not add much to the strength of the hydrated cement as a bond of the aggregate. Thus a hydrated neat specimen containing relatively much colloid would have a comparatively low strength when compared with one containing more crystalline products of hydration. This different character of hydration would, as measured by the strength of the richer sand specimens, possibly be but slight, while in a concrete the cement with a low neat strength would give a high strength. Consequently it would not seem as if there should be any fixed relation between the strength developed by cements as neat, mortar, or concrete test pieces. This does not always appear to be true in respect to Portland cements. But it should be remembered that the majority of the latter do not differ much among themselves in composition or physical properties, and consequently those which develop high testing mortars also develop high testing concretes at the same periods. When, however, extremes in compositions or physical properties are compared, then it is found that one producing a high-strength mortar may produce a low-strength concrete, and vice versa.

A noticeable feature is brought out when the tensile specimens of neat and mortar are compared. It is readily seen that the mortars of the cements high in alumina (Nos. 1, 2, and 8) at comparatively early periods develop higher strengths than the neat specimen. This becomes more marked at the late periods. At the three-year periods, cements Nos. 1, 2, and 8 without plaster

develop in this order, as neat test pieces, tensile strength of 225, 255, and 000 pounds per square inch. As 1:3 mortar at the same period they develop tensile strength of 715, 605, and 615 pounds. An examination of Table 6 reveals that the neat test pieces of these three cements developed their highest strength at either 24 hours or 7 days, after which there was a retrogression, whereas the mortars have gained strength rather consistently. It would appear as if the hydration of the former had been very complete at those early periods. Their continued storage in water had permitted of the absorption of water by the hydrated colloidal material to such a degree that the strength was decidedly reduced. Such an action would be similar to the absorption of excess water by fish glue or any other organic glue whereby the cementing properties of these are reduced to a minimum or destroyed completely. On the other hand, the hydration of the mortars was less, access of water to the interior of the test piece having been slower on account of the impervious nature of the sand grains.

The other cements do not show this unusual condition of a mortar having a greater strength than the neat cement from which it was made. However, these others contain silica, combined either as the orthosilicate or as the ternary silica-lime-alumina compound, $2CaO.Al_2O_3.SiO_2$. The former hydrates very slowly and to but a comparatively slight degree, although at the end of a year it will have attained almost as great a strength as a normal Portland cement. The ternary compound has not been noticed to harden in this laboratory. The gain in strength of the neat specimens of these cements containing the larger amounts of silica is due therefore to the hydration of the orthosilicate, which manifests itself at the late ages and offsets the loss in strength of those containing but the small amounts of silica.

When discussing the matter of "setting," there was pointed out the marked effect produced on the aluminates by the use of plaster of Paris. The latter caused such a decided acceleration of the time of set as to render the cements almost unusable. The use of this material also produced the undesirable effect of reducing the strength. This is not very marked with certain forms of test pieces, as the tension briquettes, or with certain cements, as those high in silica. Also the effect was not as marked at some periods as others, as shown by the mortars tested at early periods in compression. But generally the plaster was undesirable not only on

account of producing too quick a set but also usually reducing the strength.

The principal feature of the strength data, however, is the high strength developed at early ages by the mortars and concretes, especially by those cements high in alumina. Those containing the larger amounts of silica do not show such high initial strengths but, on the other hand, show a greater increase in strength with age. The ideal composition considered both from economy in cost of raw materials and general qualities of the cement produced therefrom would appear to be exhibited by cements No. 4 or 7. Their composition is such as would permit of the use of relatively impure alumina or limestone, or the use of a quantity of kaolin or low iron-oxide clay in place of all alumina. The resulting product would have the desired early hardening property in addition to the one of exhibiting a continuous increase in strength over a long period.

The cause of the high early strength and the relatively small increases with age can be inferred from previous remarks dealing with the hydration of the aluminates. This hydration is not only rapid but more thorough than with Portland cements. There is therefore produced more of the cementing agent, which in this case is both the hydrated tricalcium aluminate and the hydrated alumina, both in a colloidal form and comparatively insoluble. In the case of Portland cement the only aluminate present—the tricalcium aluminate—does not split off any of the hydrated alumina, and the silicates form a hydrated silicate and lime hydrate. The latter, compared with hydrated alumina, is relatively soluble, and when it does separate out of solution it forms the crystals so noticeable in specimens of set Portland cement. Therefore in the latter cements only part of the hydrated compounds formed have cementing properties, while with the aluminates, all of the products of hydration not only have cementing properties but they are furthermore developed very rapidly. This difference not only accounts for the difference in the early strength but also for the rate of increase in strength.

A microscopical examination was made of the various specimens after breaking at the three-year period. In general, it may be said that the largest amounts of unhydrated cement were noticed in the neat specimens, the next in the sand specimens, and the least amount in the concrete. The concrete stored in the air was markedly different from that stored in the damp closet,

the difference being plainly evident macroscopically in the more chalky appearance of the former. Also under the microscope the former showed more unhydrated cement, and the hydrated products were more amorphous or else the crystals were much more poorly developed. The sand specimens also showed a better crystallization than the neat ones, but possibly not as much as the concrete cured in the damp closet. The crystalline products were the tricalcium aluminate, a little hydrated lime in some cases, and some tricalcium sulphoaluminate. At the end of three years the ternary compound ($2CaOSiO_2Al_2O_3$) was still unhydrated, and in several cases the orthosilicate was noticed only partially hydrated. The same was true of the monocalcium aluminate. The amount of tricalcium sulphoaluminate was strikingly small even if the cement had been mixed with plaster. It was noticed usually in cavities and in specimens made from cement No. 5 in particular. It was also noticed in several specimens made from unplastered cement in cavities near the exterior where undoubtedly the sulphate had been taken from the tap water in which they were stored. The crystals were long but very small in cross section and appeared in tuft-like masses which had no mechanical strength. Many times the amount actually noted in any cavity would have been necessary before any disruptive force could have been generated.

The fact that the concretes contained more crystalline products of hydration than the neat specimens should not be used as an argument against the theory advanced above to explain the difference in the adhesive and cohesive properties developed by a cement. While the concrete did contain more crystalline hydrated material, the cement as a whole was also more completely hydrated, so that the percentage of crystals in the hydrated material was actually less in the concretes than in the neat test pieces.

SUMMARY

There have been produced in a rotary kiln certain cements, characterized by a high alumina content, which have the property of hardening in a short time to such a degree as to give very high strengths. This is especially true when the cements are used in mortars or concrete.

The temperatures necessary for burning the raw mixes and the actions of these in the kiln were little if at all different from those observed in the burning of Portland cement.

The raw materials used were limestone and calcined alumina; in some cases the effects of such impurities as silica and iron oxide were studied by the use of kaolin, bauxite, or flint, in addition to the above.

The ground clinker in some cases set very rapidly, but in other cases where the alumina was very high it set slowly.

The hardening was very rapid in all cases unless the content of impurities became very high, when the hardening resembled more closely that of Portland cement.

The predominant constituent noted in the clinker was the monocalcium aluminate or the 3:5 calcium aluminate. As the silica increased, increasing amounts of the orthosilicate of lime or the ternary compound $2CaO.SiO_2.Al_2O_3$ were noted.

The products of hydration were hydrated tricalcium aluminate and hydrated alumina resulting from the aluminates, and hydrated lime from the orthosilicate of lime, leaving the latter in a hydrated form but of a lower lime content than that required to form $2CaO.SiO_2$.

The early hardenings were due to the rapidity with which the aluminates hydrate. The high strengths were due to the thoroughness of the hydration and to the fact that this was largely colloidal.

The methods of storage of the test pieces showed that these cements had their strengths rather materially reduced by the absorption of moisture. This was due to the large amount of colloidal products of hydration, which are very susceptible to moisture changes. They would therefore not be satisfactory for use when subjected to the action of water.

The cost of the raw materials at the present time is such as to preclude the commercial use of these cements except under very special cases. They are of much interest, however, in showing that besides the high-limed silica compounds there is another group of compounds in the lime-alumina-silica system which has cementing qualities. This investigation showed, however, that these two groups are the only ones of this character in the system.

WASHINGTON, February 14, 1921.